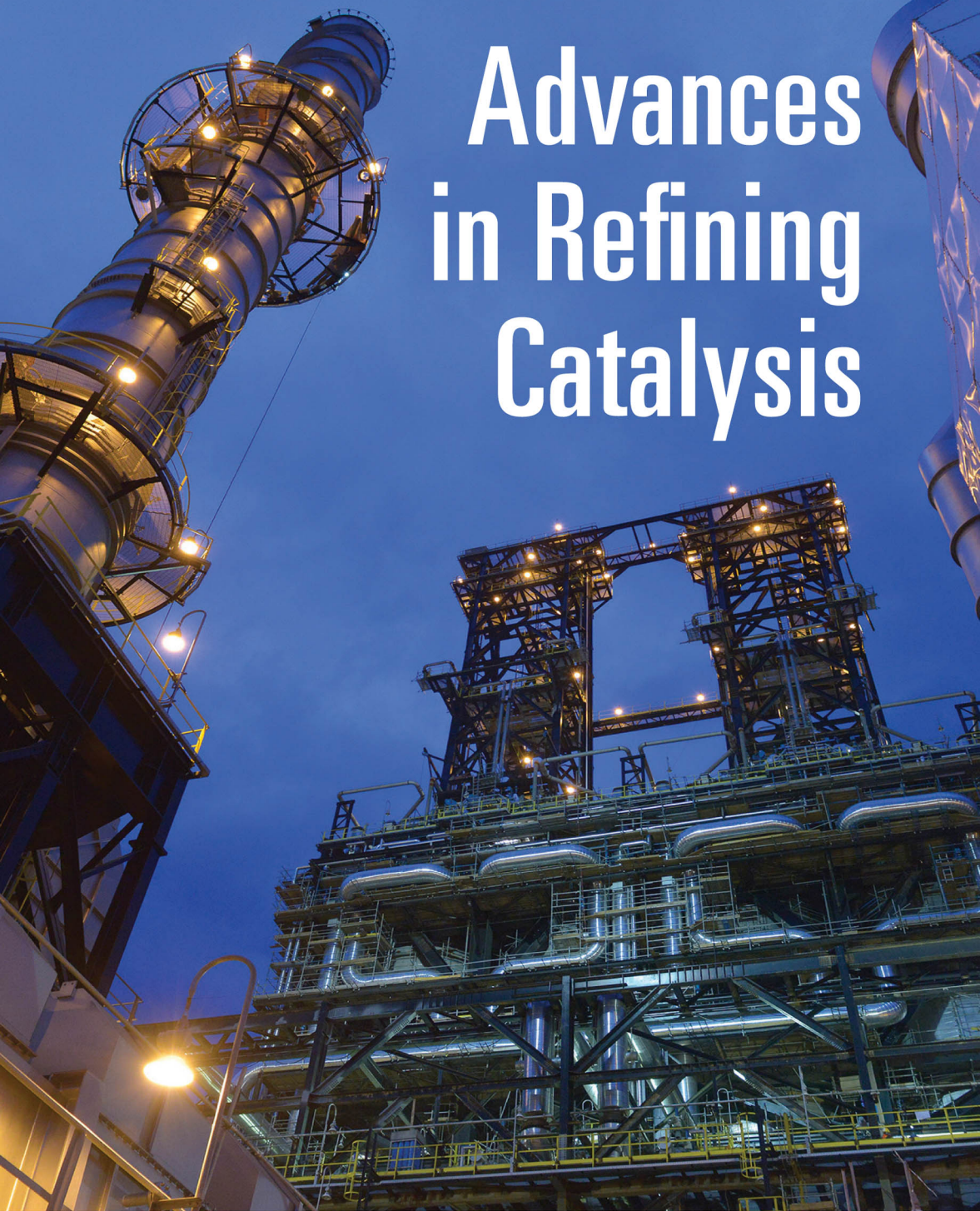


CHEMICAL INDUSTRIES

Advances in Refining Catalysis



CRC Press
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Edited by **Deniz Uner**

Advances in Refining Catalysis



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Advances in Refining Catalysis

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CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
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CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Printed on acid-free paper
Version Date: 20161208

International Standard Book Number-13: 978-1-4987-2997-0 (Hardback)

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Library of Congress Cataloging-in-Publication Data

Names: Üner, Deniz, editor.

Title: Advances in refining catalysis / edited by Deniz Üner.

Description: New York : Routledge, [2017] | Includes bibliographical references and index.

Identifiers: LCCN 2016029763 | ISBN 9781498729970 (hardback)

Subjects: LCSH: Catalysis. | Catalytic reforming. | Chemical engineering.

Classification: LCC TP156.C35 A35 2017 | DDC 660/.2995--dc23

LC record available at <https://lcn.loc.gov/2016029763>

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Preface

Oil refining is not a trivial technology. The raw material is complex in composition and prone to price fluctuations, driven by global and local politics. The technology developments in this field are rather slow to take shape and take effect due to the large scales of economies involved. The investments are very large, and it takes several years to pay back. Therefore, technology changes are not as quickly reflected as in other industries, such as automotive and electronics. The economics of the refinery operations depend mainly on the efficiency of the design, skills of the engineers in the field, and last but not the least, the quality of the catalysts used. This volume intends to bring together some of the developments in the refining catalysis taking place when the oil price fluctuations were at their peak. While the evolving and emerging trends in selected refinery operations are emphasized, two different perspectives on the concept of biorefinery are also presented. In Chapter 10, a thorough review of the recent literature on catalysis for biomass conversions is presented. In Chapter 11, a perspective for integrating the biorefineries into existing value chain from the point of view of catalysis can be found.

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Acknowledgments

This book has its origin in the Refinery Engineer Training Program (RAYEP) and the related project that was conducted under its auspices between the Middle East Technical University Chemical Engineering Department and TUPRAS—Turkish Petroleum Refineries Co. I would like to express my thanks to general directors Yavuz Erkut, who passed the torch (or the flare) at the end of 2015 to Ibrahim Yelmenoglu, and on their behalf to all who contributed to make this volume possible. My appreciation extends to all members of the METU RAYEP team, particularly Prof. Erdogan Alper, from whom I learned immensely about refining and refinery engineering.

This volume came to shape during my sabbatical at the Chemical and Biomolecular Engineering Department of the University of California Berkeley. First and foremost, I am grateful to my host and the Department Chair Prof. Jeffrey A. Reimer for his invitation and making my sabbatical a truly enriching experience. I thank Prof. Enrique Iglesia for stimulating discussions in and outside the classrooms of the Chemical Reaction Engineering and Catalysis courses during the 2015–2016 academic year, Prof. Alexander Katz for his contagious enthusiasm in catalysis, Prof. Alexis T. Bell for his refined wisdom, and last but not the least Prof. John M. Prausnitz, who is a great mentor in his gentle presence. I also would like to thank Prof. Halil Kalipcilar, the chair of the Chemical Engineering Department at the Middle East Technical University, for making my sabbatical at UC Berkeley a pleasant journey.

It is my hope that the positive changes brought about in the twentieth century by the internal combustion engine technology and its driving force—oil—will be surpassed by the advances-in-the-making of the twenty-first century. Our efforts are for the children of our children.



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Section I

Refining Technologies Outlook



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1 Advances in Refining Technologies

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Jeffery C. Bricker, Xin Zhu, and Maureen Bricker*

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1.1 INTRODUCTION

Although oil price fluctuations have recently slowed capital investments, the fundamental long-term market drivers for growth of fuels and petrochemicals are still very strong, for example, the growth of middle class. By 2030, 3 billion people are expected to enter the middle class, mostly in emerging markets, and create demand for quality fuels and products derived from petrochemicals. This chapter discusses key refining advances as well as petrochemical integration including shale gas, high-quality fuels, renewables, energy efficiency, and refinery–petrochemical integration.

With worldwide petroleum refining capacity expected to grow steadily for several decades, breakthrough new technologies will offer a competitive advantage for early adopters, allowing improved high-quality fuel production for transportation as well as potential petrochemical integration. Clean, high-quality fuels produced in high yields will remain a primary focus, driven by environmental legislation requirements and better economics. These technology advancements can be accomplished by development of new process technology often made possible by breakthroughs in new catalytic materials as discussed in this chapter.

More rapid petrochemical demand growth rates relative to demand for fuels create new opportunities for refiners to improve value generation by adding petrochemical feedstock production to their product slate. We expect that the multinational climate agreement from Paris negotiations in 2015 should lead to a longer-term expansion of renewable content into transportation fuels. As discussed in this chapter, technology for advanced fuels from renewable hydrocarbon sources has been commercialized successfully.

Although the market fluctuations may modify techno economic choices by refiners, the overall strategy to implement the most economic, efficient, and environmentally

sustainable technologies creates the best opportunities for growth and profitability in the refining industry.

1.2 FUEL QUALITY

This section will focus on the fundamentals of important catalyst design considerations.

Presently, various environmental regulations stipulate a low level of sulfur and in some cases a low level of aromatic composition in both gasoline and diesel products, which has spurred a growth in a variety of hydroprocessing complexes around the world. As the sulfur level required in gasoline and diesel reached low levels approaching zero, a large increase in both hydrotreating and hydrocracking capacity grew in the world, and is still projected to grow over the next decade.¹ Even when a refiner in a certain area of the world does not need the stringent specification for their region, the process is designed for the stiffer requirement so that the refiner is able to export their products to any area of the world.

Hydrocracking and hydrotreating are the two major technologies that allow refiners to meet fuel specifications. There have been excellent recent reviews of the overall technology.²

1.2.1 HYDROCRACKING

Hydrocracking is a flexible catalytic refining process that is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils, including residue. The process adds hydrogen, which improves the hydrogen-to-carbon ratio of the net reactor effluent, removes impurities like sulfur to produce a product that meets the environmental specifications, and converts the heavy feed to a desired boiling range. The chemistry involves the conversion of heavy molecular weight compounds to lower molecular weight compounds through carbon-carbon bond breaking and hydrogen addition. Hydrocracking feeds can range from heavy vacuum gas oils (VGOs) and coker gas oils to atmospheric gas oils to blends of the combination of VGO, light cycle oils (LCOs), coker gas oils, and tar sands products. The demand for hydrocracking is predicted to be a stable growth market at 6%.

1.2.2 FLOW SCHEMES

Hydrocracking units can be configured in a number of ways. The unit can consist of one or two reactors with either one or multiple catalysts. The process can use one or two stages and be operated in once-through or recycle mode. The choice of the configuration depends on the feed properties and the specific product slate desired by the refiner. The five main types of operating units are mild, moderate/medium pressure, conventional, partial conversion, and resid hydrocracking. These are shown in Table 1.1.

As described in Section 1.2.4, the reaction section fulfills two functions: pretreating/hydrotreating and hydrocracking. This is shown in Figure 1.1 as separate reactors, though both functions can be achieved in a single reactor when using some types

TABLE 1.1
Types of Hydrocracking Processes

Unit Type	Typical Conversion	Total Pressure (bar/psig)	Hydrogen Partial Pressure (bar/psig)	Reactor Temperature (°C/°F)
Mild (MHC)	20–40	60–100/870–1450	20–55/290–840	350–440/662–824
Moderate/medium pressure	40–70	100–110/1450–1600	50–95/725–1380	340–435/644–815
Conventional	50–100	110–200/1600–2900	95–140/1390–2030	340–435/662–842
Resid Hydrocracking (LC-finishing)	65–100	97–340/1400–3500	73–255/1050–2625	385–450/725–914

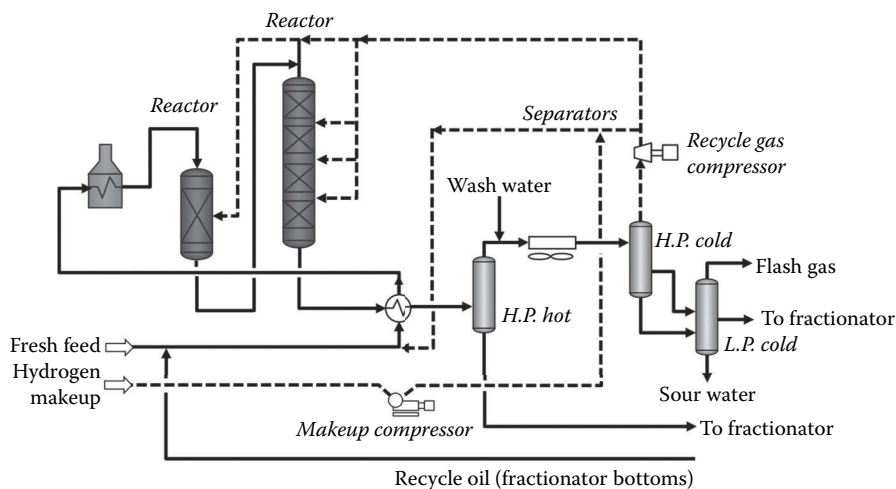


FIGURE 1.1 Typical flow diagram of reactor section of single-stage hydrocracking unit.

of catalysts, e.g., an amorphous catalyst. In most modern configurations, different catalysts are used for the hydrotreating and the hydrocracking sections. However, both types of catalyst can be loaded in the same reactor; separate vessels are not needed. When using both pretreatment and cracking configurations, the first catalyst (a hydrotreating catalyst) converts organic sulfur, oxygenates, and nitrogen from hetero compounds in the feedstock to hydrogen sulfide, water, and ammonia, respectively. The deleterious effect of gas phase H_2S and NH_3 on hydrocracking catalysts is considerably less than that of the corresponding organic hetero compounds in the liquid phase.^{3,4} The hydrotreating catalyst also facilitates the hydrogenation of aromatics. In the single-stage configuration, the products from the hydrotreating reaction zone are passed over a hydrocracking catalyst where most of the hydrocracking takes place. The conversion occurs in the presence of NH_3 , H_2S , and small amounts

of unconverted hetero compounds. The hydrotreating catalyst is designed to convert the hetero compounds in the feedstock. Typically, such catalysts comprise sulfided molybdenum and nickel on an alumina support. The reactor operates at temperatures varying from 570°F to 800°F (300–425°C) and hydrogen pressures between 1250 and 2500 psig (85–170 bar). Under these conditions, heteroatom elimination, significant hydrogenation, and some cracking also take place. The cracking catalyst operates at the same hydrogen pressures but at temperatures varying from 570°F to as high as 840°F (300–450°C) for amorphous hydrocracking catalysts and up to 825°F (440°C) for zeolite-containing catalysts.

1.2.3 TWO-STAGE RECYCLE HYDROCRACKING

The two-stage hydrocracking process configuration is also widely used, especially for large capacity units. In two-stage units, the hydrotreating and some cracking take place in the first stage. The effluent from the first stage is separated and fractionated, with the unconverted oil passing to the second stage for further reaction. The reactor effluent from the second stage reaction section goes back to the common fractionator. A simplified schematic of a two-stage hydrocracker is shown in Figure 1.2. The key point is that the catalyst in the second stage may be operating in the near absence of ammonia and hydrogen sulfide. Thus, the catalysts used in the second stage need to be tailored for that reaction environment to maximize desired product selectivity.

1.2.4 CHEMISTRY

The chemistry of hydrotreating and hydrocracking is commonly taken together and termed hydroprocessing and is similar for both sections of the hydroprocessing unit. Hydrotreating converts heteroatoms, and hydrocracking converts higher carbon number feed molecules to lower molecular weight products by cracking the side chains and by saturating the aromatics and olefins. Hydrocracking catalysts will also

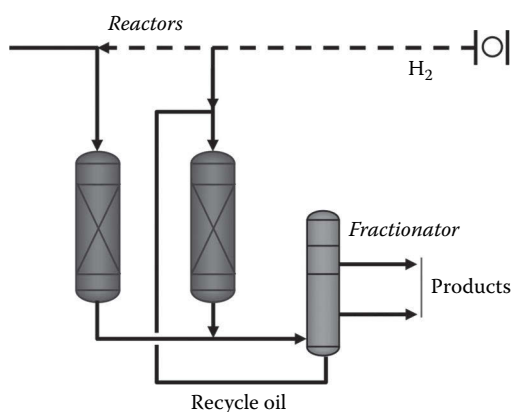


FIGURE 1.2 Two-stage hydrocracking.

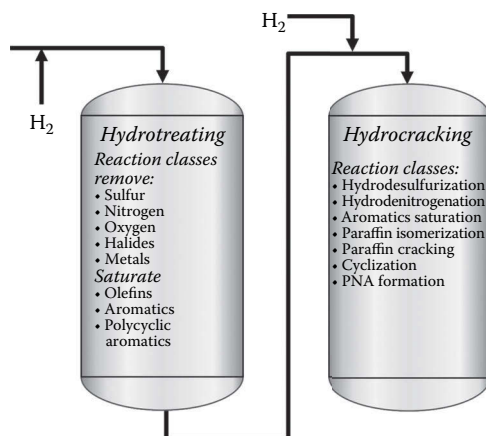


FIGURE 1.3 Summary of hydroprocessing reaction classes in the sections of the hydrotreating and hydrocracking reactors.

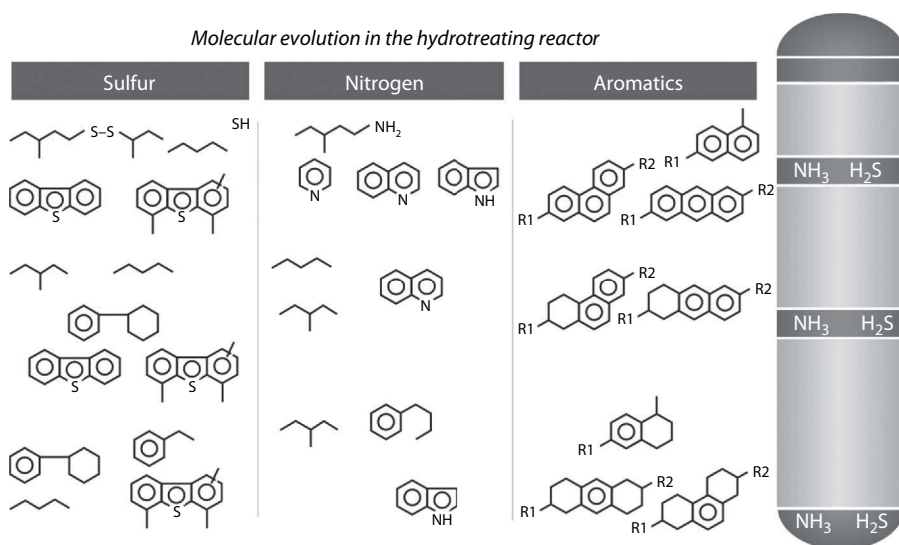


FIGURE 1.4 Evolution of the reactions in the hydrotreating reactor.

remove any residual sulfur and nitrogen, which remain after the hydrotreating. The evolution of the reaction profile between the hydrotreating reactor and the hydrocracking reactor is shown in Figures 1.3 through 1.5.

1.2.5 HYDROTREATING REACTIONS

The hydrotreating reactions proceed in the following order: metal removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal, and halide removal

and aromatic saturation. Figure 1.4 shows the evolution of the reactions in the hydrotreating reactor. Hydrogen is consumed in all of the treating reactions.

1.2.6 HYDROCRACKING REACTIONS

Hydrocracking reactions proceed through a bifunctional mechanism.⁵⁻⁹ Two distinct types of catalytic sites are required to catalyze the separate steps in the reaction sequence. The first function is the acid function, which provides for cracking and isomerization, and the second function is the metal function, which provides for olefin formation and hydrogenation. The cracking reaction requires heat, while the hydrogenation reaction generates heat. Figure 1.5 shows the evolution of the reactions in the hydrocracking reactor. Overall, there is a heat release during hydrocracking reactions; the heat release is a function of the hydrogen consumption, where higher hydrogen consumption will generate a larger temperature increase. Generally, the hydrogen consumption in hydrocracking (including the pretreating section) is 1200–2400 SCFB (200–420 Nm³/m³) resulting in a typical heat release of 50–100 Btu/SCF H₂ (2.1–4.2 kcal/m³ H₂), which translates into a temperature increase of about 0.1°F/SCF H₂ consumed. This includes the heat release generated in the hydrotreating section.

In general, the hydrocracking reaction starts with the generation of an olefin or a cyclo-olefin on a metal site on the catalyst. Next, an acid site adds a proton to the olefin or cyclo-olefin to produce a carbenium ion. The carbenium ion cracks to a smaller carbenium ion and a smaller olefin. These products are the primary hydrocracking products. These primary products can react further to produce still smaller

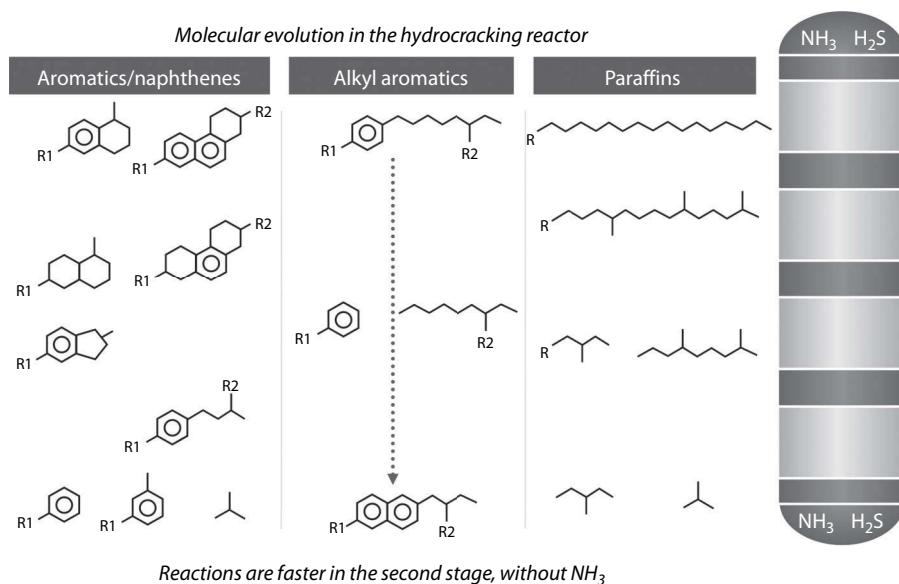


FIGURE 1.5 Evolution of the reactions in the hydrocracking reactor.

secondary hydrocracking products. The reaction sequence can be terminated at primary products by abstracting a proton from the carbenium ion to form an olefin at an acid site and by saturating the olefin at a metal site. Figure 1.6 illustrates the specific steps involved in the hydrocracking of paraffins. The reaction begins with the generation of an olefin and the conversion of the olefin to a carbenium ion. The carbenium ion typically isomerizes to form a more stable tertiary carbenium ion. Next, the cracking reaction occurs at a bond that is beta to the carbenium ion charge. The beta position is the second bond from the ionic charge. Carbenium ions can react with olefins to transfer charge from one fragment to the other. In this way, charge can be transferred from a smaller hydrocarbon fragment to a larger fragment that can better accommodate the charge. Finally, olefin hydrogenation completes the mechanism. This selectivity is due in part to a more favorable equilibrium for the formation of higher carbon number olefins. In addition, large paraffins adsorb more strongly. The carbenium ion intermediate causes extensive isomerization of the products, especially to *n*-methyl isomers, because tertiary carbenium ions are more stable. Finally, the production of C_1 to C_3 is low because the production of these light gases involves the unfavorable formation of primary and secondary carbenium ions. Other molecular species such as alkyl naphthenes, alkyl aromatics, and so on react via similar mechanisms, e.g., via the carbenium ion mechanism.

The hydrocracking reactions tend to favor conversion of large molecules because the equilibrium for olefin formation is more favorable for large molecules, and because the relative strength of adsorption is greater for large molecules. In hydrocracking, the products are highly isomerized, C_1 and C_3 formation is low, and single rings are relatively stable.

In addition to treating and hydrocracking, several other important reactions take place in hydrocrackers. These are aromatic saturation, polynuclear aromatics (PNAs) formation, and coke formation. Aromatic saturation is the only reaction in hydrocracking that is equilibrium-limited at the higher temperatures reached by hydrocrackers toward the end of the catalyst cycle life. Because of this equilibrium limitation, complete aromatic saturation is not possible toward the end of the catalyst cycle when reactor temperature has to be increased to make up for the loss in catalyst activity resulting from coke formation and deposition.

PNAs, sometimes called polycyclic aromatics (PCAs), or polyaromatic hydrocarbons (PAHs), are compounds containing at least two benzene (BZ) rings in the molecule. Normally, the feed to a hydrocracker can contain PNAs with up to seven BZ rings in the molecule. PNA formation is an important, though undesirable, reaction that occurs in hydrocrackers. Figure 1.7 shows the competing pathways for conversion of multiring aromatics. One pathway starts with metal-catalyzed ring saturation and continues with acid-catalyzed cracking reactions. The other pathway begins with an acid-catalyzed condensation reaction to form a multiring aromatic compound. This molecule may undergo subsequent condensation reactions to form a large PNA.

The consequence of operating hydrocracking units with recycled oil is the creation of large PNA molecules that can contain more than seven aromatic rings in the molecule. These are called heavy PNAs (HPNAs) whose formation is due to condensation reactions of smaller PNAs on the catalyst surface. The HPNAs produced on

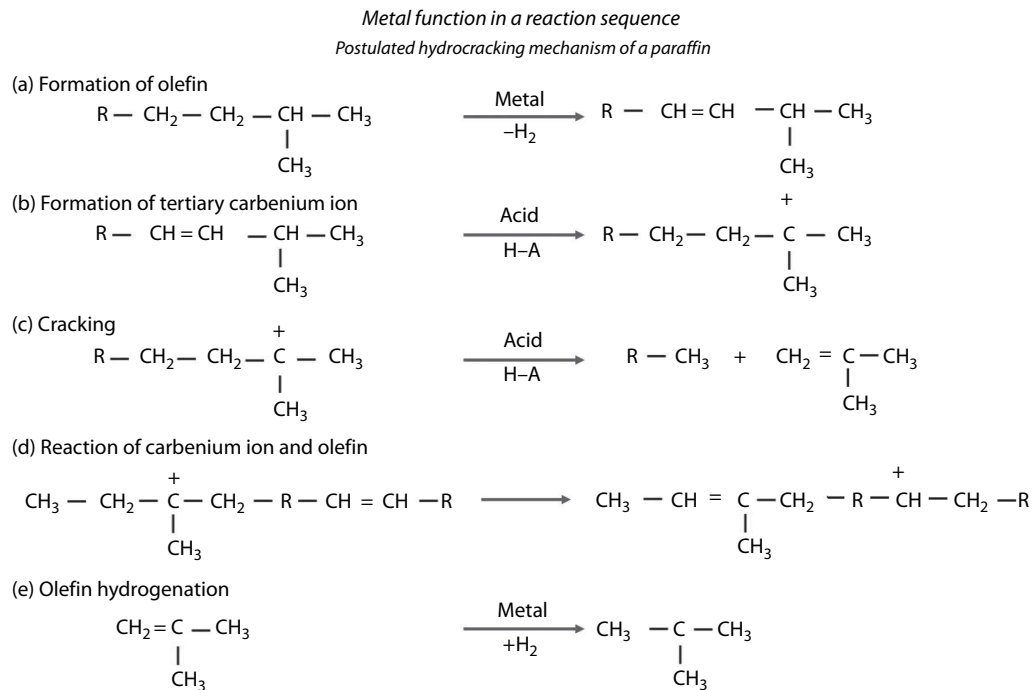


FIGURE 1.6 Steps involved in the hydrocracking of paraffin molecules.

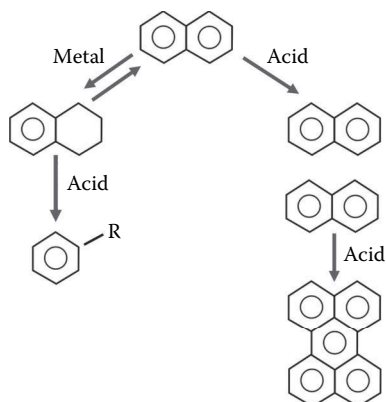


FIGURE 1.7 Possible pathways for multi-ring aromatics.

the catalyst may exit the reactor and cause downstream equipment fouling, or they may deposit on the catalyst and form coke, which deactivates the catalyst.

1.2.7 CATALYSTS

Hydrocracking catalysts are dual functional.¹⁰ Both metallic dehydrogenation/hydrogenation sites and acidic sites must be present on the catalyst surface for the cracking reaction to occur as well as some of the other reactions such as hydroisomerization and dehydrocyclization.

The acidic support consists of amorphous oxides (e.g., silica-alumina), a crystalline zeolite such as a (modified Y zeolite) plus binder (e.g., alumina), or a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support. The metals providing the hydrogenation function can be noble metals (palladium, platinum) or non-noble (also called “base”) metal sulfides from group VIA (molybdenum, tungsten) and group VIIIA (cobalt, nickel). As previously discussed, these metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation.

The ratio between the catalyst’s cracking function and hydrogenation function can be adjusted in order to optimize activity and selectivity.

For a hydrocracking catalyst to be effective, it is important that there be a rapid molecular transfer between the acid sites and hydrogenation sites in order to avoid undesirable secondary reactions. Rapid molecular transfer can be achieved by having the hydrogenation sites located in the proximity of the cracking (acid) sites.

1.2.8 ACID FUNCTION OF THE CATALYST

A solid oxide support material supplies the acid function of the hydrocracking catalyst. Amorphous silica-alumina (ASA) provides the cracking function of amorphous catalysts and serves as support for the hydrogenation metals. Sometimes, ASA

catalysts or a combination of ASA and zeolite can be used to produce high-yield distillate hydrocracking catalysts. ASA also plays a catalytic role in low-zeolite catalysts. Zeolites are commonly used in high activity distillate-selective catalysts and in hydrocracking catalysts for the production of naphtha.

Amorphous mixed metal oxide supports are acidic because of the difference in charge between adjacent cations in the oxide structure. The advantages of ASA for hydrocracking are pores, which permit access of bulky feedstock molecules to the acidic sites, and moderate activity, which makes the metal–acid balance needed for distillate selectivity easier to obtain.

Zeolites are used in hydrocracking catalysts because they provided high activity due to their higher acidity compared to the ASA materials. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework; cations and water are located in the pores. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen atoms. When the cations in zeolites are exchanged with ammonium ion and calcined, an acidic material can be formed.

One zeolite used in hydrocracking, Y zeolite, has a structure nearly identical to the naturally found zeolite Faujasite.⁹ The Y zeolite has both a relatively large free aperture, which controls access of reactants to acid sites, and a three-dimensional pore structure, which allows diffusion of the reactants in and products out with minimal interference. Both Bronsted and Lewis acids are possible in zeolites. The number and the strength of the acid sites can be varied in various synthesis steps. These sites are highly uniform, but each zeolite may have more than one type of site. The following factors influence the number and strength of acid sites in zeolites:

- The types of cations occupying the ion exchange sites
- Thermal treatments of the zeolite
- The framework silica-to-alumina ratio in the zeolite

For example, Y zeolite can be treated to modify the Si/Al ratio; common methods to accomplish this are either a thermal or a hydrothermal treatment. Figure 1.8 shows an image after hydrothermal treatment of stabilized Y zeolite. When aluminum is removed, the total number of acid sites is decreased because each proton is associated with framework aluminum. As can be seen in Figure 1.8, there is also a generation of mesoporosity in the zeolite. However, the reduction of the alumina sites increases the strength of the acid sites of the remaining alumina to a certain point. As a result, the total acidity of the zeolite, which is a product of the number of sites and strength per site, peaks at an intermediate extent of dealumination. The crystallinity of the zeolite can also be modified depending on the treatment history. The acid site concentration and strength of the zeolite will affect the final hydrocracking catalyst properties.

1.2.9 CATALYST MANUFACTURING

Hydroprocessing catalysts can be manufactured by a variety of methods. The method chosen usually represents a balance between manufacturing cost and the degree to

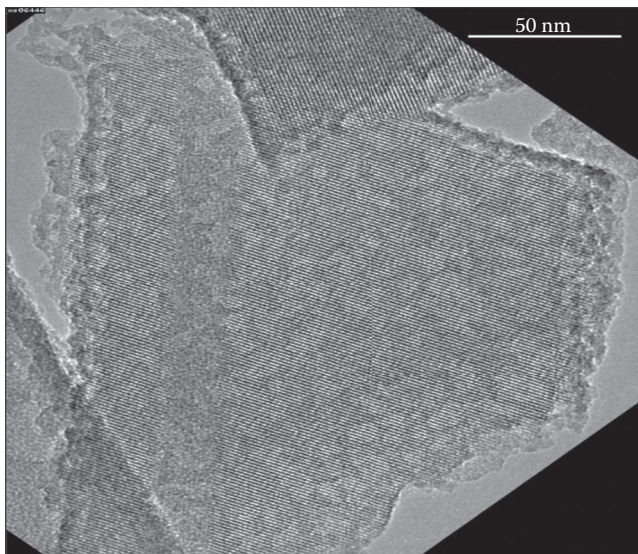


FIGURE 1.8 Stabilized Y after thermal treatments.

which the desired chemical and physical properties are achieved. While the chemical composition of the catalyst plays a decisive role in its performance, the physical and mechanical properties also play a major role. The preparation of hydroprocessing catalysts involves several steps, the details of which are usually trade secrets of catalyst producers, but include precipitation, filtration (decantation, centrifugation), washing, drying, forming, calcination, and metal impregnation.

1.2.10 CATALYST ACTIVATION

Base metal hydrocracking catalysts have to be prepared in the final state through a sulfiding procedure in order to create the active species, the metal sulfides. Several names are used for this treatment, such as sulfiding or pre-sulfiding. The metals on the greatest majority of catalysts are in an oxide form at the completion of the manufacturing process.

Noble metal catalysts are activated by hydrogen reduction of the finished catalyst, in which the metal is also in an oxide form.

The active phase is similar for the CoMo or NiMo supported on Al_2O_3 or SiO_2 and by analogy Ni/W on the more complex hydrocracking catalyst.¹⁰ These consist of Co or Ni atoms on the edges of MoS_2 slabs and are referred to as CoMoS and NiMoS phases, and by analogy NiWS phase. W and Mo exhibit different behavior with respect to sulfidation. Ni/W is more difficult to sulfide than Ni/Mo, i.e., requires higher temperature. The presence of the Ni enhances the sulfidation of either Ni or Mo. The slabs of Mo or S have a specific length and appear as strands with different levels of stacking. An image¹¹ of Ni/W in a hydrocracking catalyst is shown in Figure 1.9. In this figure, the individual atoms of W can be seen.

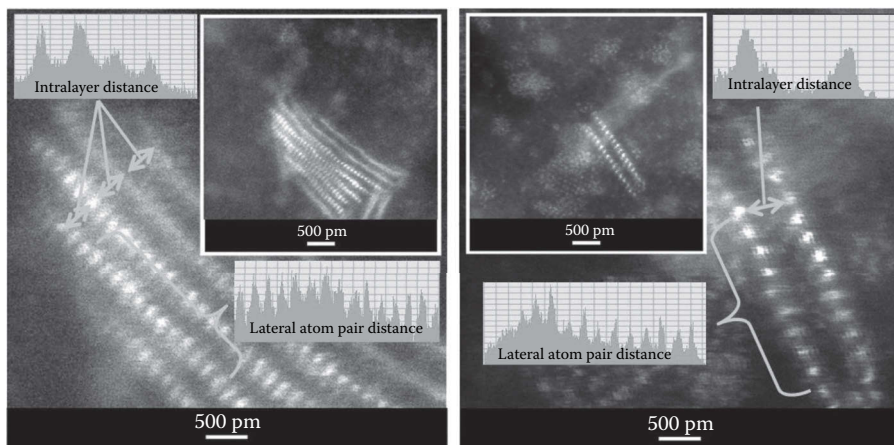


FIGURE 1.9 Image of NiWS active phase using UOP aberration-corrected Titan 80-300 Super X electron microscope.

Sulfiding is accomplished mainly in situ, though some refiners have started to do the activation outside the unit (*ex situ*). More and more refiners will opt to receive the catalyst at the refinery site in pre-sulfided state to accelerate the start-up of the unit. In situ sulfiding can be accomplished either in vapor or liquid phase. In vapor phase sulfiding, the activation of the catalyst is accomplished by injecting a chemical that easily decomposes to H_2S , such as dimethyl-disulfide (DMDS) or di-methyl-sulfide (DMS).

1.2.11 SUMMARY

The growth in clean fuels has led to a strong growth in hydroprocessing technologies. The core of hydroprocessing technologies are the catalysts, which can be designed for ultrahigh activity for heteroatom removal with selective cracking to distillate, jet, or naphtha depending on the refiner needs. The catalyst design and reactor stacking takes into account the cascading reactions, which must all be catalyzed efficiently for the optimum reactor yields, run length, and product quality. UOP has invested heavily in hydroprocessing tools including pilot plants, advanced material characterization, new materials, and catalysis to be the leading provider of hydroprocessing technology in the world today.

1.3 IMPACT OF SHALE OIL ON FUTURE REFINING

The US shale crude boom of 2010–2014 has been tempered in 2015 by lower crude oil prices. Nonetheless, it is anticipated that, worldwide, light shale crudes will play an important role as traditional crude supply/demand comes back into balance. This section attempts to explore some of the opportunities and challenges associated with shale crudes, aka tight shale oil.

Tight shale crude is typically characterized as light and sweet with a very different yield pattern for refined products, as well as contaminant levels, impacting the

refiners' processing units and product slate. Tight oil crudes typically have higher light and heavy naphtha yields, presenting increasing challenges to the naphtha complex, typically consisting of naphtha hydrotreating (NHT), light naphtha isomerization, and UOP CCR™ Platforming units. Advances, discussed herein, in each of these technologies are important for refiners to capture the value of shale oil.

1.3.1 MARKET OVERVIEW

The US supply of domestic natural gas liquids and crude was drastically impacted by improvements in hydraulic fracturing technology.¹² The supply of natural gas was first impacted, resulting in a price decrease, which presented refiners with a lower cost fuel and feedstock for hydrogen. The second major application of hydraulic fracturing technology was to recover liquid hydrocarbons from existing shale plays, which were previously uneconomical.

Production of tight shale oil from these fields had increased rapidly such that North Dakota is now the second largest producer of crude oil in the United States (US EIA data). The recently issued BP World Energy Outlook estimated that US tight shale oil production could add as much as 5 MMBPD by 2030.¹³ Worldwide, abundant shale oil deposits have been discovered as shown in Figure 1.10 and will prove to be an important resource in the future.

1.3.2 TIGHT OIL CRUDE YIELDS SHIFT TOWARD LIGHTER HYDROCARBONS

The crude assay reflects the yield pattern and is key information for determining the refinery products. Shown in Figure 1.10 are yields of liquified petroleum gas (LPG), naphtha, kerosene, diesel, VGO, and vacuum residue for several crudes with varying American Petroleum Institute (API) gravities. Table 1.2 provides key crude properties for the tight shale and conventional crudes. The tight oil crudes, Bakken, Eagle Ford, and Utica, are typically lighter crudes, have higher API, and have predominantly higher LPG and naphtha with less heavy VGO and vacuum residue material. The general trends for tight oils (high API) are as follows:

- Lower sulfur, nitrogen contaminants
 - Lower H₂ demand for hydrotreating and hydrocracking units
- Lower vacuum residue yield
 - Lower VGO, coker, and fluid catalytic cracking (FCC) rates
 - Lower FCC rates, lower C₃⁼/C₄⁼ to alkylation unit, less alkylate
 - Less FCC naphtha, alkylate in gasoline pool
- Higher paraffin concentration
 - Diesel cut: higher cetane number with poorer cold-flow properties
 - Naphtha cut: leaner reformer feed, lower C₅₊ and H₂ yields
- Higher light and heavy naphtha yields
 - Larger increase in light naphtha; isomerization feed rates increase
 - Increase in feed rate to platforming unit (fixed bed or CCR)
 - Higher quantity of isomerate and reformate in gasoline pool

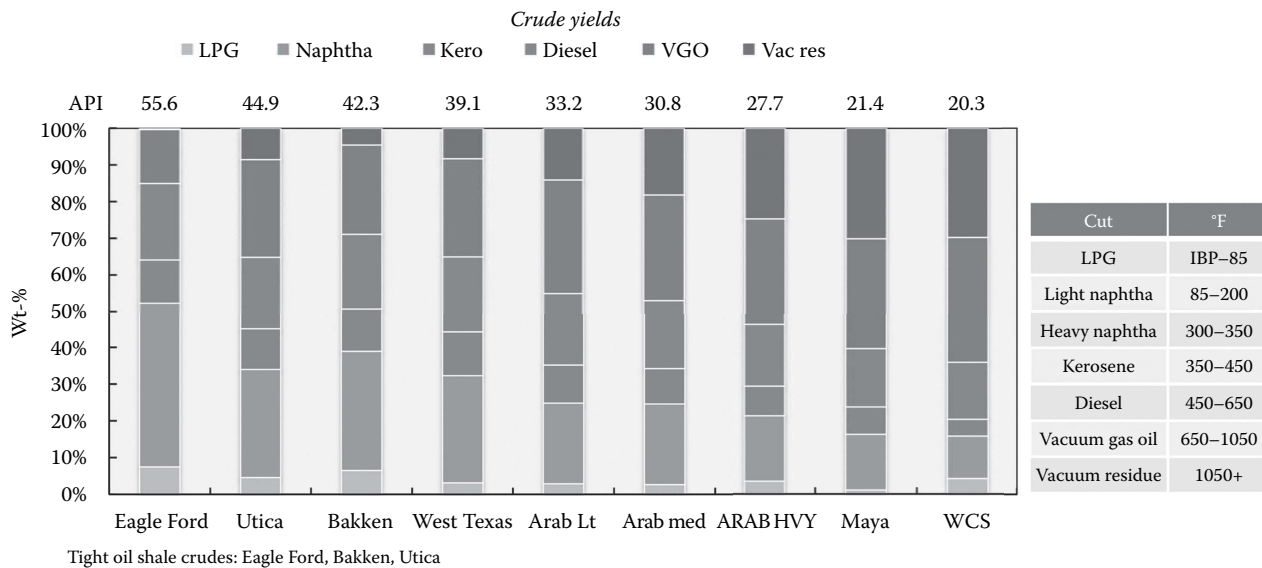


FIGURE 1.10 Crude yields (wt%).

TABLE 1.2
Crude Properties

	Units	Western Canada		Arab	WTI	Bakken	Eagle Ford
		Select	Maya	Med			
API GRAVITY	API	20.3	21.4	30.8	39.1	42.3	46.5
Sulfur	wt%	3.3	3.5	2.6	0.3	0.1	0.1
Neut of TAN No.	mgKOH/g	0.8	0.1	0.3		0.0	0.1
Nitrogen	ppm	2770	3573	1210	1000	500	41
Hydrogen	wt%	11.4	12.1	12.7	13.3	13.8	14.3
Rams bottom carbon	wt%	9.0	11.2	5.6		0.8	0.0
Iron	ppm	8	5	4		2	1
Vanadium	ppm	118	286	34		0	0
Nickel	ppm	49	53	10		1	0

A linear program published in a 2014 UOP study was used to evaluate the refinery-wide impact when switching to a lighter tight oil feed slate.^{14,15}

1.3.3 NAPHTHA COMPLEX OVERVIEW

A simplified schematic of the naphtha complex is shown in Figure 1.11. Hydrotreated feed from the NHT is sent to the naphtha splitter; the lighter C_5/C_6 paraffins are sent to the isomerization unit and the heavier C_{7+} to the CCR Platforming unit. Controlling the gasoline pool BZ level is a key specification, impacting the naphtha complex

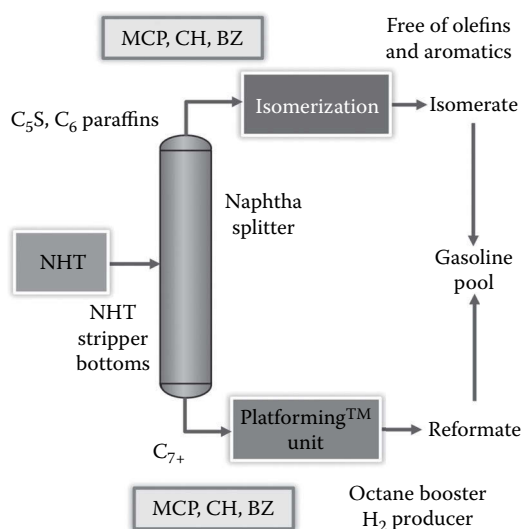


FIGURE 1.11 Naphtha complex.

design. The naphtha splitter is designed for BZ control, splitting the BZ precursors (methycyclopentane [MCP], cyclohexane [CH], and BZ) either to the isomerization or CCR Platforming unit. When BZ production is targeted, BZ precursors are sent to the reformer unit. If minimum BZ is targeted, then the BZ precursors would be sent to the isomerization unit, which is excellent for BZ saturation and conversion to high-octane C_6 paraffins.

Removing the C_6 components from the Platforming unit feed has many advantages. First, a higher C_{7+} feed rate can be achieved to the CCR Platforming unit. Second, since C_6 components are among the hardest to reform, the CCR Platforming unit severity is reduced. Third, the BZ concentration of the reformate product is greatly reduced.

Processing the C_5 and C_6 components in an isomerization unit allows the refiner to recover lost octane due to BZ reduction.

1.3.3.1 Optimizing the NHT Unit—Catalyst Improvements

Catalyst improvements have allowed refiners to increase feed rate and/or reduce utilities. UOP has introduced two new catalysts, HYT-1118 for straight-run, low nitrogen feeds and HYT-1119 for cracked stocks and high nitrogen feeds.

HYT-1118 catalyst is UOP's latest-generation cobalt molybdenum hydrotreating catalyst, building upon the proven performance of UOP's S-120 catalyst. HYT-1118 catalyst provides the benefits of higher hydrodesulfurization (HDS) and hydrodenitri-fication (HDN) activity while being more than 30% less dense than the previous-generation S-120 catalyst.

UOP's HYT-1119 is a robust catalyst designed for use in NHT applications to remove sulfur and nitrogen compounds with cracked stocks and high nitrogen feeds. HYT-1119 has high stability due to high pore diameter and pore volume, resulting in long catalyst life. In addition, standard regeneration methods can be used to minimize catalyst life-cycle costs.

Shown below are the features and benefits of HYT-1119:

- Improved metal distribution
- 20% higher surface area for higher silicon pickup
- No phosphorus for increased stability and higher silicon pickup
- Lower aromatic saturation
- Reduced loaded density for lower fill cost
- Higher HDS and HDN activity

1.3.4 ISOMERIZATION

Light naphtha, C_5 – C_6 , from the naphtha splitter overhead is sent to the isomerization unit. UOP offers several isomerization designs in which the product research octane number clear (RONC) can range from ~82 to ~92.

- UOP Par-IsomTM Process design: ~82–85 RONC
- UOP PenexTM Process design: HOT Penex—Hydrogen Once Through ~82–85 RONC
- UOP PenexTM design with recycle: ~87–92 RONC

1.3.4.1 Par-Isom Unit with PI-242 or PI-244 Catalyst

The Par-Isom unit uses PI-242 or PI-244 (lower Pt) catalyst, while the Penex unit uses a chlorided alumina-type catalyst. The PI-242/244 catalyst is robust to water and sulfur upsets and does not require a high chloride concentration; consequently, driers and caustic scrubbing for chloride removal are not required, reducing capital expenditures (CAPEX). Both processes can produce 82 to 85 RONC without a liquid recycle.

UOP PI-242 and UOP PI-244 Par-Isom catalyst features and benefits:

- UOP's PI-242 or PI-244 offers an alternative to chlorided alumina catalyst with nearly equivalent selectivity and activity along with tolerance to contaminants such as sulfur and water.

Fully regenerable and long life.

- Use of UOP Par-Isom catalyst can reduce the required catalyst volume from 10% to up to 50% compared to competitive products, thus reducing the fill cost. For new units, UOP Par-Isom catalyst can reduce catalyst and Pt fill cost by 58% and 63% respectively, along with reduction in CAPEX and operating expenditures (OPEX).

1.3.4.2 Penex Process with I-122, I-82 I-84 Chlorided Alumina Catalysts

A benefit of the Penex low coking tendency is that the unit could be designed for "Hydrogen Once Through" (HOT). In the HOT Penex process, recycle gas is not required, thus eliminating the need for a product condenser, product separator, stabilizer feed/bottoms exchanger, and recycle gas compressor. The lower equipment and utility costs significantly lower CAPEX and OPEX, and is the current standard design for Penex units. The product RONC is 83–85 RONC for a single hydrocarbon pass.

1.3.4.3 UOP I-82 and UOP I-84 Penex Catalysts

I-82 catalyst is the highest activity, light paraffin isomerization catalyst commercially available. The catalyst is an amorphous, chloride alumina catalyst containing platinum and is a robust product for maximizing isomerate octane-barrels. I-82 is optimized for the UOP Penex process and is particularly suited for feedstocks that contain a high concentration of BZ and C₆₊ cyclic hydrocarbons. The catalyst selectively converts normal butane, pentane, and hexane to higher octane branched hydrocarbons. In addition, I-82 saturates BZ and is designed to operate over a wide range of reaction conditions and feedstocks.

I-84 catalyst (0.18% Pt) is an extension of I-82 catalyst (0.24 wt% Pt), but with 25% lower platinum concentration and is suited for feedstocks that have moderate levels of BZ and C₆₊ cyclic hydrocarbons.

The yield and RONC/motor octane number clear (MONC) benefits are dependent upon the X factor of the feed as shown in Figure 1.12. The performance benefit can be significant for I-82, for all X factors, which improved the product value from \$6 million/year (base case) to \$12 million/year (case 2) for the highest X factor feeds.¹⁶

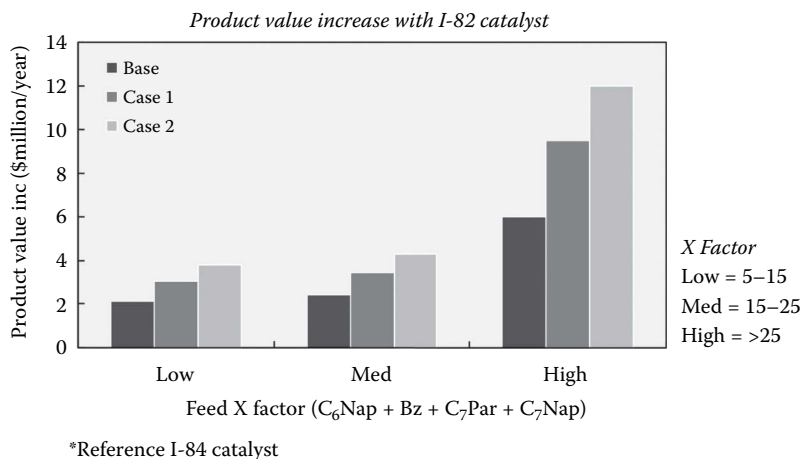


FIGURE 1.12 Product value increase with I-82 with varying X factor feeds.

The higher isomerate RONC-barrels (BBLs) allowed the CCR Platforming unit to decrease severity and increased C₅₊ yields.

1.3.5 CCR PLATFORMING UNIT

Heavy naphtha, C₇₊–C₁₁, from the naphtha splitter bottoms is sent to the CCR Reformer unit. The heavy naphtha is reformed to convert paraffins and naphthenes to an aromatics-rich reformate and hydrogen. Shown in Figure 1.13 is the process flow for the CCR Platforming unit.

1.3.5.1 Process Flow

Hydrotreated straight-run naphtha is mixed with recycle hydrogen, then preheated by exchange with reactor effluent in the combined feed exchanger. The combined feed is raised to the reaction temperature in the charge heater and sent to the reactor section. The predominant reactions are endothermic; consequently, an interheater is used between each reactor to reheat to the reaction temperature.

Catalyst flows vertically by gravity down a reactor stack of three to four reactors. Over time, coke builds up on the catalyst and requires regeneration. Coked catalyst is continually withdrawn from the bottom of the last reactor in the stack and transferred to UOP's CycleMax™ CCR™ regenerator for catalyst regeneration, consisting of four steps: coke burning, oxychlorination, drying, and reduction. The first three steps of coke burning, oxychlorination, and drying occur in the regeneration tower, while the fourth step, reduction, occurs in the reduction zone on top of the first reactor in the reactor stack.

1.3.5.2 CCR Platforming Catalyst Options

UOP continues to develop new CCR Platforming catalysts to address customers' demands and deliver higher performance. UOP has an extensive catalyst portfolio, addressing various customers' needs for motor fuel and/or aromatics production.

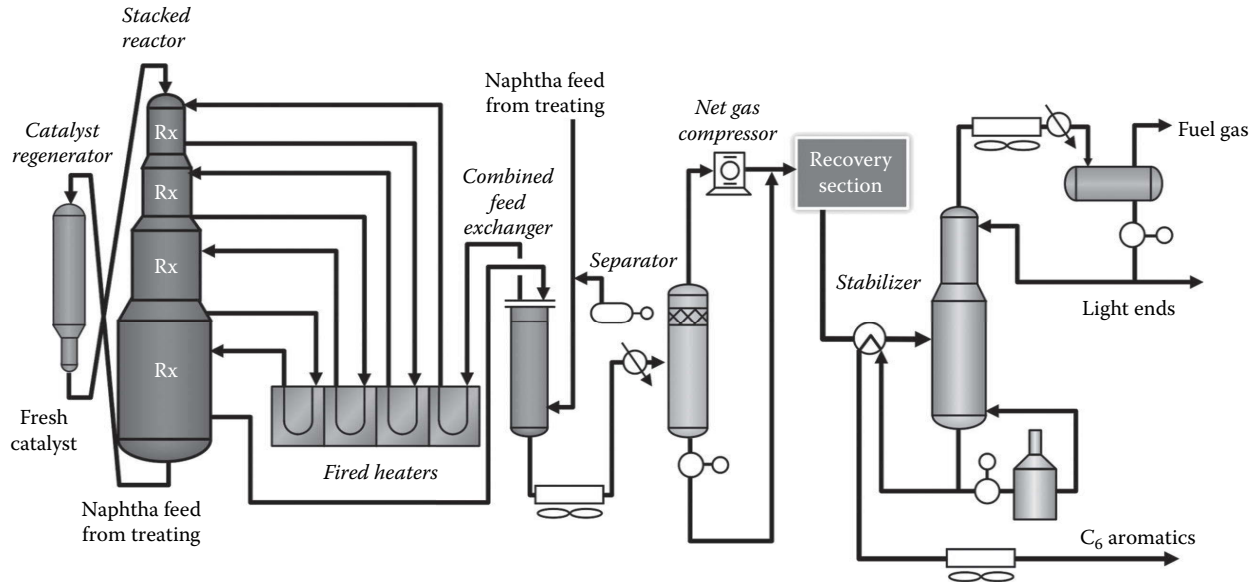


FIGURE 1.13 CCR Platforming unit process flow.

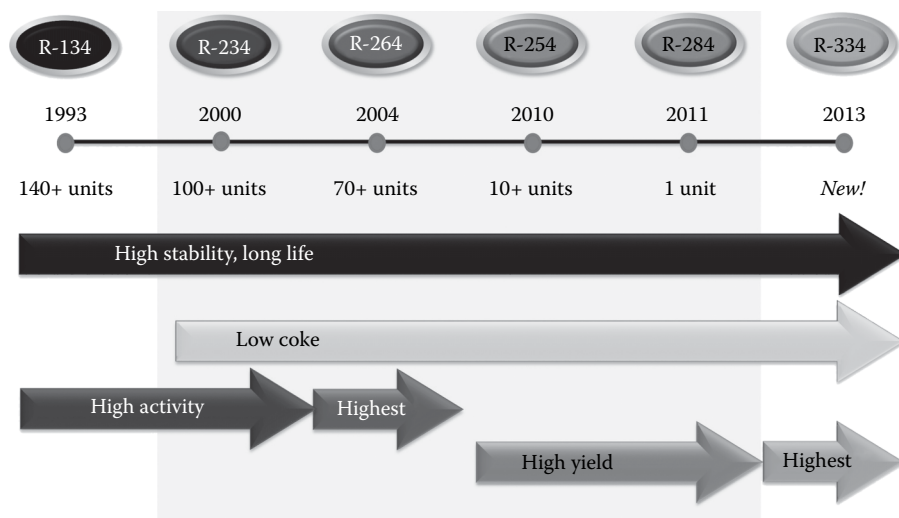


FIGURE 1.14 UOP CCR Platforming catalyst innovations.

Figure 1.14 shows the evolution of UOP's CCR Reforming catalyst: R-134TM, R-234TM, R-264TM, R-254TM, R-284TM, and the new R-334TM catalyst.

The R-130 series catalyst was first commercialized in 1993. Features of the R-130 series catalyst are high activity (lower reactor inlet temperatures), good surface area stability, and chloride retention.

Due to changes within the market, a low coke R-234 catalyst, was developed, providing an initial 20–25% lower coke make and higher C₅₊ yield versus R-134 catalyst. R-234 catalyst also maintained the excellent surface area stability and chloride retention as the R-130 series catalyst.

R-264 catalyst was developed specifically for customers who targeted to increase throughput to their unit. The R-264 is a high-yield, higher-density catalyst, providing an increased reactor pinning margin. For BZ/toluene/xylene (BTX) operation, the unit could be operated at a higher feed rate, and coupled with the higher activity, maximum BTX is produced.

UOP also developed promoted catalyst, R-254 and R-284 catalysts, both providing significantly higher yields. There are over 10 units operating with R-254 catalyst and others with R-284 catalyst.

UOP's latest catalyst offering is R-334 catalyst, designating the first 300 series product. The R-334 catalyst is UOP's highest yield catalyst and also features long life, low coke. Table 1.3 shows the catalyst properties for R-234, R-254, and R-334 catalysts. It is interesting to note that the high-yield R-334 catalyst does not include a promoter, obtaining the optimal performance by proprietary base and manufacturing technique.

1.3.6 MAXIMIZING PROFITABILITY WITH HIGH-YIELD R-334 CATALYST

The high-yield R-334 catalyst reduces cracking, decreasing fuel gas, LPG, and C₅'s. Table 1.4 quantifies the benefits of higher yields with R-334 catalyst for 75% Eagle

TABLE 1.3
CCR Catalyst Properties

Catalyst	R-234	R-254	R-334
Sphere		Sphere	
Pill diameter		1/16 inch (1.6 mm)	
Surface area		180 m ² /g	
Density (ABD)		36 lb/ft ³ (560 kg/m ³)	
Pt level		0.29 wt%	
Crush strength		50 + N	
Promoter	No	Yes	No

TABLE 1.4
R-334 Yield Benefits

		R-234	R-334
Case		2	
Crude		Eagle Ford/WCS	
Feed rate	BPD	39,317	39,317
Reformate	RONC	101.3	101.3
P	Lv-%	75	75
N	Lv-%	16	16
A	Lv-%	9	9
Product yields			Delta
H ₂	SCFB	1775	90
Fuel gas	wt%	2.57	-0.52
C ₃	Lv%	2.33	-0.53
C ₄	Lv%	2.8	-0.6
C ₅	Lv%	2.1	-0.47
C ₅₊	Lv%	80.9	1
C ₅₊ RVP	psi	2.1	-0.2
RONC—bbls		Base	39,825

Ford/25% WCS. The feed composition and feed rate were kept constant, but the catalyst was changed from R-234 catalyst to R-334 catalyst. The benefits of R-334 catalyst include higher yield, but in addition, the reduced cracking reduces C₅'s, decreasing the reformate Reid vapor pressure (RVP) by 0.2 psig (1.4 kPa). The reduction in RVP allows additional 110 BPD of C₄'s to be blended into the gasoline pool while maintaining the 9 psig (62 kPa) RVP target.

The key to these advanced CCR catalysts are the control of olefin cyclization versus cracking to light ends. An extensive body of mechanistic work on catalytic reforming has been published¹⁶ with an overall mechanism shown in Figure 1.15.

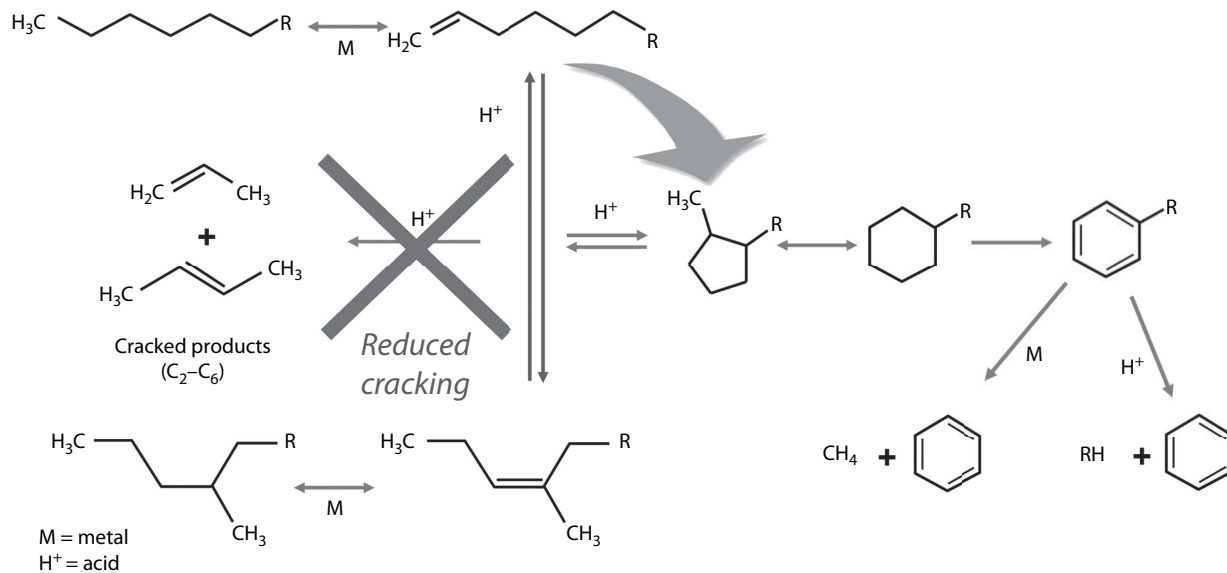


FIGURE 1.15 Schematic of a mechanism for reforming over a bifunctional Pt–alumina catalyst.

Early studies used pure components to probe the reaction chemistry.¹⁷ High liquid hourly space velocity (LHSV) testing allowed the identification of primary cyclic olefin products in conversion of CH and MCP.¹⁸ The bifunctional nature of catalytic reforming has been investigated using the conversion of MCP to BZ. This reaction has been studied as a function of catalyst acid and metal content, with the result that the acid-catalyzed naphthene isomerization step was identified as rate-controlling.¹⁹

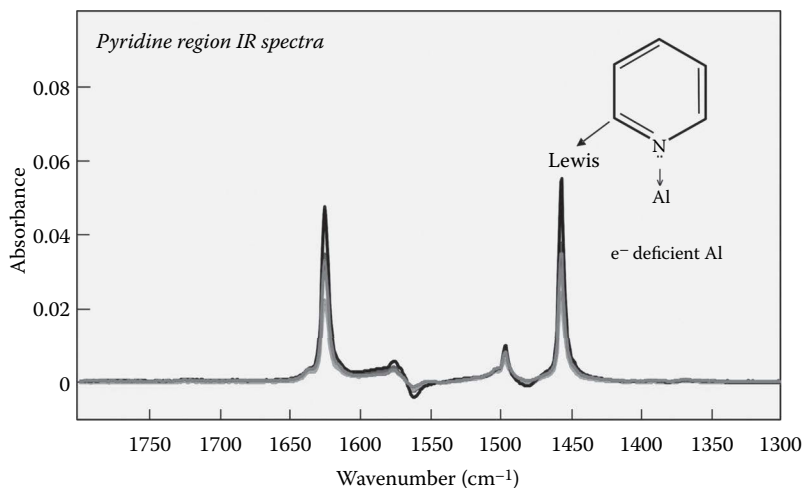
Dehydrogenation reactions that form olefins and aromatics are highly endothermic, and the large heat of reaction for reforming is an important consideration in the design of reactor systems. Paraffin isomerization is relatively neutral, while cracking reactions are exothermic. Table 1.5 shows the heats of reaction for the main reforming reactions for carbon number 6.²⁰ Formation of aromatics is thermodynamically favored and provides a driving force for paraffin and naphthene conversion. This is particularly important for conversion of five-membered ring naphthenes, as five-membered ring naphthenes are thermodynamically favored over six-membered ring naphthenes under reforming conditions.

Mechanistic studies of ring opening of MCP have contributed to the understanding of the role of metal and acid sites in both paraffin dehydrocyclization and naphthene conversion in reforming.^{21,22} Studies have included rate measurements with hydrogen partial pressure, water addition, nitrogen and sulfur poisoning, and mixed catalyst experiments. Olefins are believed to be key intermediates for isomerization, cracking, and aromatization. Olefin cyclization has also been specifically studied over alumina and supports promoted with halides.^{23,24} The results indicate that diolefins are not intermediates in cyclization for Pt-alumina catalysts under typical reforming conditions.²⁵ The key to the new UOP R-334 catalyst is the selectivity to cyclization of olefins to naphthenes, with reduced cracking to light ends as shown in Figure 1.15. R-334 achieves this through a reduction in strong Lewis acid sites while maintaining moderate acid sites ideal for cyclization on the support as shown in Figure 1.16 as measured by pyridine infrared spectroscopy (IR).

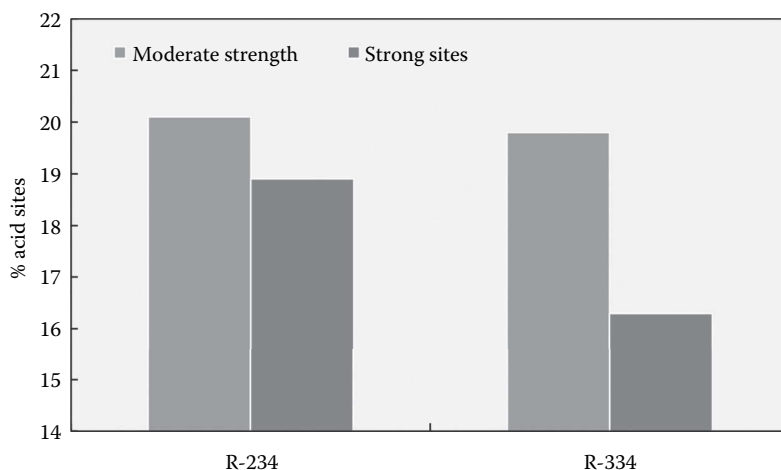
TABLE 1.5
Thermodynamic Data for Reforming Reactions

Reaction	K_p^a at 500°C for P_i in MPa	ΔH , kJ mol ⁻¹ of Hydrocarbon
Cyclohexane \rightleftharpoons Benzene + 3H ₂	6×10^8	221
Methylcyclopentane \rightleftharpoons Cyclohexane	0.086	-16
<i>n</i> -Hexane \rightleftharpoons Benzene + 4H ₂	8.4×10^8	266
<i>n</i> -Hexane \rightleftharpoons 2-Methylpentane	1.1	-5.9
<i>n</i> -Hexane \rightleftharpoons 1-Hexane + H ₂	0.37	130

^a For the reaction $(HC)_1 \rightleftharpoons (HC)_2 + nH_2$ the equilibrium constant is defined as: $K_p = \frac{P(HC)_2^{P_2} H_2}{P(HC)_1}$



(a)



(b)

FIGURE 1.16 R-334 optimizes acid site strength. (a) Pyridine IR spectra showing the Lewis acid sites, (b) is the relative strong and moderate acid sites for the two catalysts.

1.3.7 SUMMARY

Processing lower-cost tight oil shale crudes such as Bakken, Utica, and Eagle Ford can be accommodated and provides significant margin opportunity; however, it presents new challenges. With higher light naphtha yields, optimizing the naphtha complex is a key component to profitability. Profitability can be increased further when employing the latest high-yield catalysts, such as UOP HYT-1119 hydrotreating catalyst, UOP R-334 Platforming catalyst, and UOP I-82 catalyst for paraffin isomerization.

1.4 PRODUCTION OF RENEWABLE FUELS FROM TRIGLYCERIDES AND FATTY ACIDS

Global use of renewable fuels, or fuels produced from nonfossil, renewable carbon resources, has grown dramatically in the past decade²⁶ driven predominantly by governmental policy. While alternative fuels from nonfossil resources, such as ethanol from fermentation of plant carbohydrates, have been used for decades, governmental mandates promoting usage began to appear in the 2000s, which saw a consumption increase of eightfold from 1.6 million gallons in 2000 to more than 15 million gallons in 2014 in the United States alone (compiled from statistics available at Ref. 27). Supporters of renewable fuels frequently point to such issues as the cost of oil,²⁸ energy security,²⁹ and the harmful carbon emissions of fossil fuels^{30,31} as the primary rationale for their use.

While many different types of renewable fuels are currently available, and more will be in the future, this section focuses on the aspects of renewable fuels that impact *refining catalysis*. As such, while catalysis is involved in the production of ethanol, fatty acid methyl ester, and other fuel additives, we will focus on the production of hydrocarbon fuels (gasoline, diesel, kerosene, etc.) from plant and waste natural oils, such as animal tallow and used cooking oil.

1.4.1 WHY PROCESS NATURAL FATS AND OILS?

Fatty acids, triglycerides, and tall oils can be effectively used to produce diesel and jet fuel (middle distillates) because their carbon chain length roughly matches the carbon number profiles of typical petroleum diesel and jet fuels. Indeed, when the fatty acid carbon chains are saturated with hydrogen and converted into paraffins, they are chemically indistinguishable from major components of petroleum diesel and jet fuels. Several process technologies based on the concept of triglyceride, free fatty acid (FFA), or tall oil hydrotreatment have been developed to convert plant- and animal-based oils into middle distillates. Commercial installations have started up over the past few years that produce renewable diesel from triglyceride, FFAs, or tall oil feed sources, as shown in Table 1.6.^{32–40}

1.4.2 TRIGLYCERIDES AND FATTY ACIDS

Triglycerides are molecules composed of three fatty acids bound to a glycerol backbone by an ester linkage.⁴¹ They are the fundamental unit of energy storage in living organisms. When the fatty acids are no longer linked to the glycerol backbone, they are called FFAs and are composed of a nonpolar hydrocarbon chain with a polar carboxylic acid functional group. Tall oil is primarily composed of FFAs and rosin acids, and is a commercial by-product of wood pulping. General structures for triglycerides and FFAs are shown in Figure 1.17. The shorthand notation used to describe fatty acids is carbon number followed by the number of carbon–carbon double bonds, also known as the degree of unsaturation, separated by a colon (carbon number:degree of unsaturation). The fatty acid carbon chain length and the degree

TABLE 1.6
Commercial Triglyceride, FFA, and Tall Oil Hydroprocessing Installations

Company Name	Capacity (BPD)	Technology	Location	Primary Product	Start-Up Date
Neste	3900	NEXBTL™	Porvoo, Finland (1)	Diesel	2007
	3900	NEXBTL™	Porvoo, Finland (1)	Diesel	2009
	16,600	NEXBTL™	Singapore	Diesel	2010
	16,600	NEXBTL™	Rotterdam, Netherlands	Diesel	2011
Dynamic Fuels	5000 ^a	Bio-Synfining™	Geismar, LA, USA	Diesel	2010
Preem	10,000 (30% RTD ^b Co-feed)	HydroFlex™	Gothenburg, Sweden	Diesel	2010
Diamond Green Diesel	10000	Ecofining™ ^c	Norco, LA, USA	Diesel	2013
ENI	7200 ^a	Ecofining™ ^c	Venice, Italy	Diesel	2014
AltAir Fuels	2500	Ecofining™ ^c	Paramount, CA, USA	Jet Fuel	2016

^a Denotes production capacity rather than feed capacity.

^b Raw tall diesel is a derivative of tall oil, in which the free fatty acids of tall oil are esterified to make fatty acid methyl esters. The rosin acids of tall oil are largely inert to esterification.

^c Ecofining™ refers to the UOP/ENI Ecofining process.

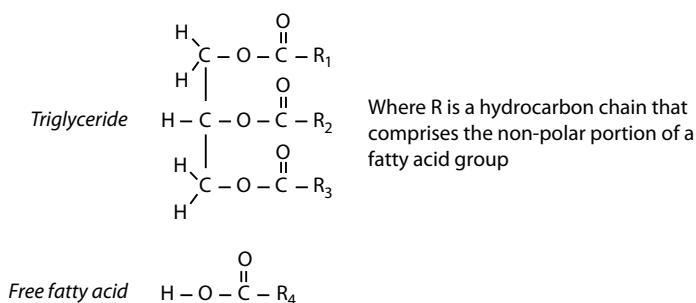


FIGURE 1.17 General structure of triglyceride and free fatty acid molecules.

of hydrogen saturation can vary significantly, usually depending on the source of the triglyceride. For example, coconut triglycerides are rich in lauric (12:0) and myristic (14:0) fatty acids, whereas soybean triglycerides are rich in oleic (18:1), linoleic (18:2), and linolenic (18:3) fatty acids. As is apparent in these two examples, fatty acids are nearly exclusively found in nature with even-numbered carbon chains of approximately 8 to 22 carbon atoms. The combination of fatty acids that can make up a triglyceride varies widely among all organisms, and can even vary, to a lesser

extent, within the same organism, depending on the season of the year, region of the world, or strain of organism. In general, most animal-derived triglycerides are more saturated than plant triglycerides. Table 1.7 shows nomenclature, carbon chain length, and degrees of unsaturation for several common fatty acids.⁴¹ Table 1.8 shows common triglyceride oil compositions in terms of the concentration of fatty acids.⁴² The method used determines the fatty acid composition by capillary column gas-liquid chromatography and provides compositions in relative (area %) values.

TABLE 1.7
Common Fatty Acids Found in Plants and Animals

Systematic Name	Trivial Name	Shorthand
Saturated Fatty Acids		
Ethanoic	Acetic	2:0
Butanoic	Butyric	4:0
Hexanoic	Caproic	6:0
Octanoic	Caprylic	8:0
Decanoic	Capric	10:0
Dodecanoic	Lauric	12:0
Tetradecanoic	Myristic	14:0
Hexadecanoic	Palmitic	16:0
Octadecanoic	Stearic	18:0
Eicosanoic	Arachidic	20:0
Docosanoic	Behenic	22:0
Monoenoic Fatty Acids		
cis-9-Hexadecenoic	Palmitoleic	16:1(n_7)
cis-6-Octadecenoic	Petroselinic	18:1(n_{12})
cis-9-Octadecenoic	Oleic	18:1(n_9)
cis-11-Octadecenoic	cis-Vaccenic	18:1(n_7)
cis-13-Docosenoic	Erucic	22:1(n_9)
cis-15-Tetracosenoic	Nervonic	24:1(n_9)
Polyunsaturated Fatty Acids^a		
9,12-Octadecadienoic	Linoleic	18:2($n-6$)
6,9,12-Octadecatrienoic	γ -Linolenic	18:3($n-6$)
9,12,15-Octadecatrienoic	α -Linolenic	18:3($n-3$)
5,8,11,14-Eicosatetraenoic	Arachidonic	20:4($n-6$)
5,8,11,14,17-Eicosapentaenoic	EPA	20:5($n-3$)
4,7,10,13,16,19- Docosahexaenoic	DHA	22:6($n-3$)

Source: Christie, W. What is a lipid? The common fatty acids of animal and plant origin. *The AOCS Lipid Library*, July 25, 2013. Web. Accessed on May 7, 2014, <http://lipidlibrary.aocs.org/Lipids/whatlip/index.htm>.

^a All the double bonds are of the cis configuration.